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Interactions Between Structure and Processing that Control Moisture Uptake in High-Performance Polycyanurates

Andrew J. Guenthner,[1] Michael E. Wright,[2] Andrew P. Chafin,[2] Josiah T. Reams,[3] Kevin R. Lamison,[3] Michael D. Ford,[3] Shawn P. J. Kirby,[4] Jacob J. Zavala,[3] Vandana Vij,[3] Joseph M. Mabry[1]

[1] Air Force Research Laboratory, Aerospace Systems Directorate, Edwards AFB, CA
[2] Naval Air Warfare Center, Weapons Division, China Lake, CA
[3] ERC Incorporated, Edwards AFB, CA
[4] California State University, Long Beach, CA 90840

Presenter: Dr. Andrew Guenthner
Air Force Research Laboratory
andrew.guenthner@us.af.mil
(661) 275-5769

24 March 2015

Outline: Basic Studies of Moisture Uptake in Cyanate Ester Networks

- **Background / Motivation**
- **SOTA Theories of Moisture Uptake in Thermosetting Networks**
- **New Tools and New Discoveries**
- **Unresolved Issues and Ways to Address Them**

Acknowledgement: Air Force Office of Scientific Research; AMG Group Members

Importance of Moisture Uptake in Composite Component Performance

Photo by U.S. Navy photo by Photographer's Mate 1st Class Anibal Rivera (public domain).

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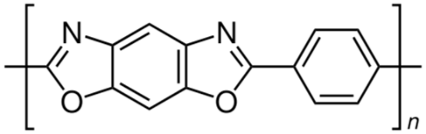

U.S. Navy photo by Mass Communication Specialist 3rd Class Torrey W. Lee (public domain)

- Water can add significantly to launch or take-off weight (3% water in composite resins = about 50 lbs of extra weight on an large SRM)
- Items with high water content can fail catastrophically when suddenly heated
- Long-term exposure to water can facilitate many mechanisms of chemical degradation, necessitating substantial "knock down" factors in design allowables
- Though more stable than epoxy resins, cyanate esters can degrade on long-term exposure to hot water

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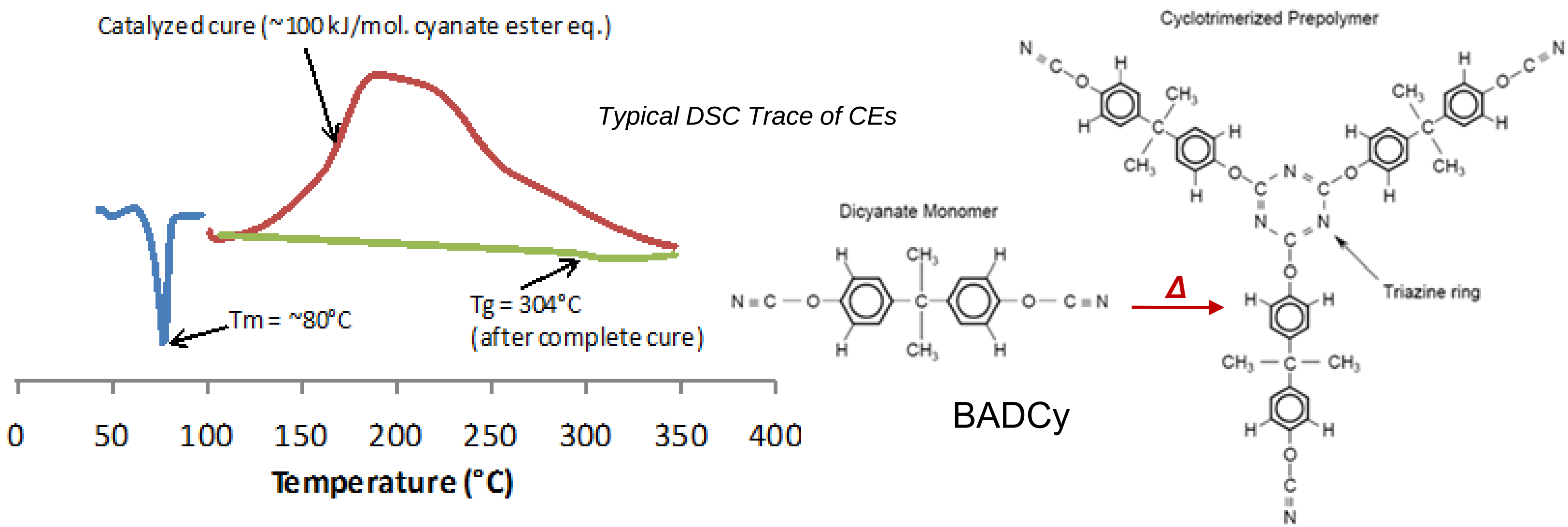
Model High-Temperature Thermosetting Polymers: Cyanate Esters



- Glass transition temperatures at full cure of 200 – 400°C
- Uncured resins exist as low-melting solids, or low to moderate viscosity liquids, making them ideal for processes such as filament winding
- Broad compatibility with co-monomers, thermoplastic tougheners, or nanoparticles for control of physical and mechanical characteristics
- Single species reaction chemistry is “cleaner” than epoxy resin and well-understood; enables development of superior predictive models for failure; readily catalyzed to cure at reasonable temperatures

Cyanate Esters: Next-Generation High-Performance Composite Resin

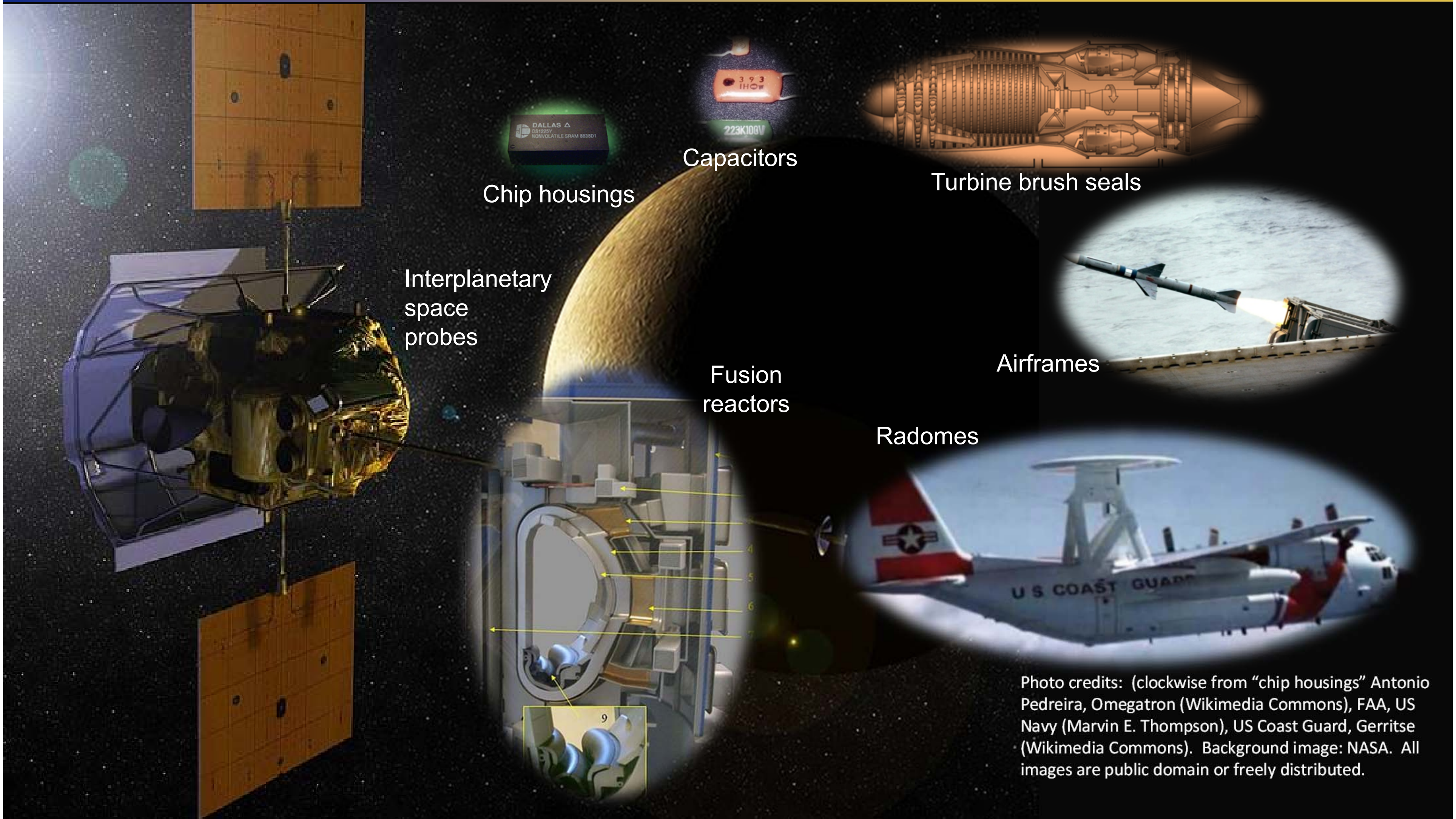
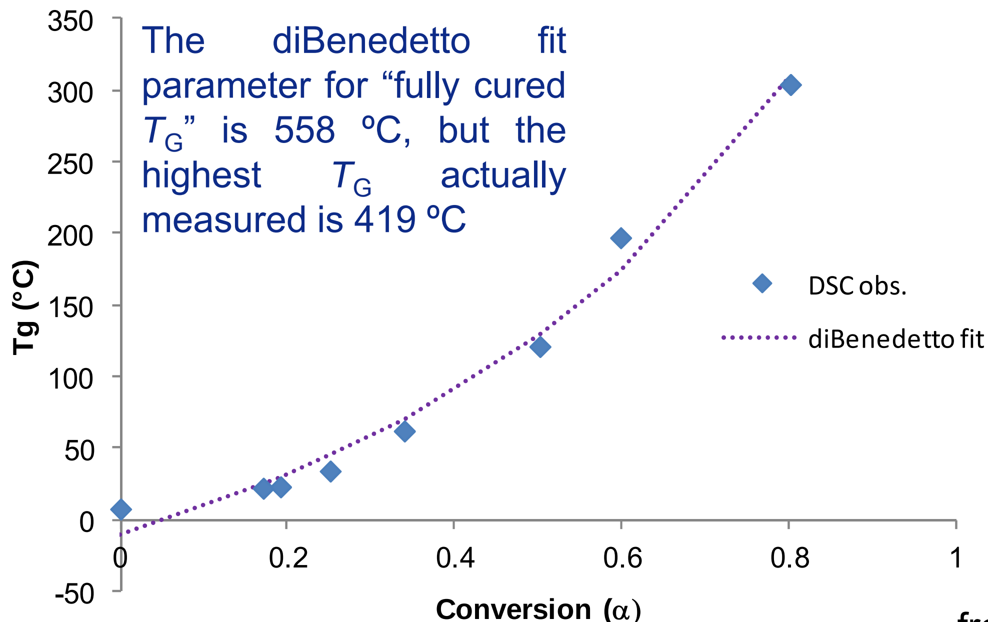
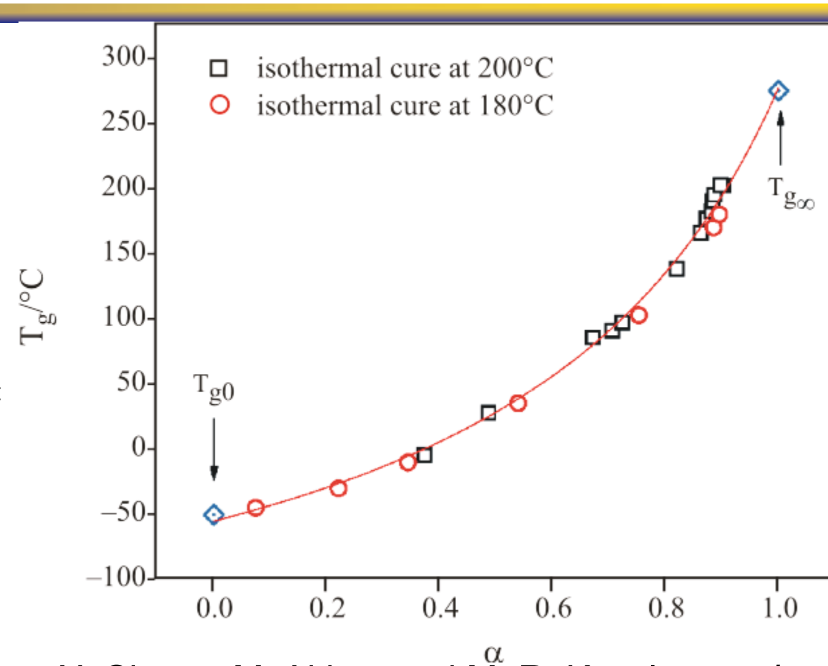


Photo credits: (clockwise from "chip housings" Antonio Pedreira, Omegatron (Wikimedia Commons), FAA, US Navy (Marvin E. Thompson), US Coast Guard, Gerritse (Wikimedia Commons). Background image: NASA. All images are public domain or freely distributed.

- Many opportunities for technical transition beyond SRM cases …

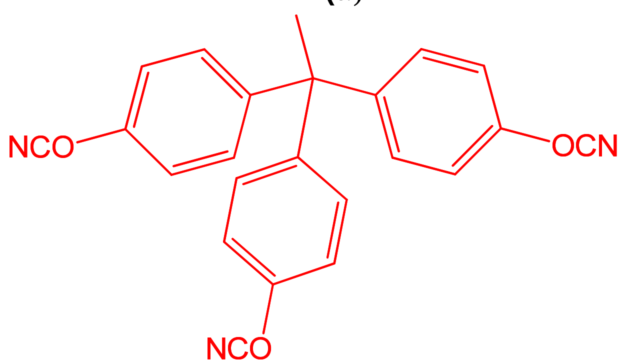
Cyanate Ester Networks: Defined by Composition and Conversion



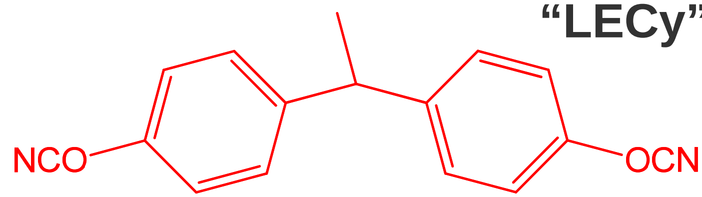


from X. Sheng, M. Akinc, and M. R. Kessler, *J. Therm. Anal. Calorim.* **2008**, *93*, 77-85 for EX-1510

"ESR255"



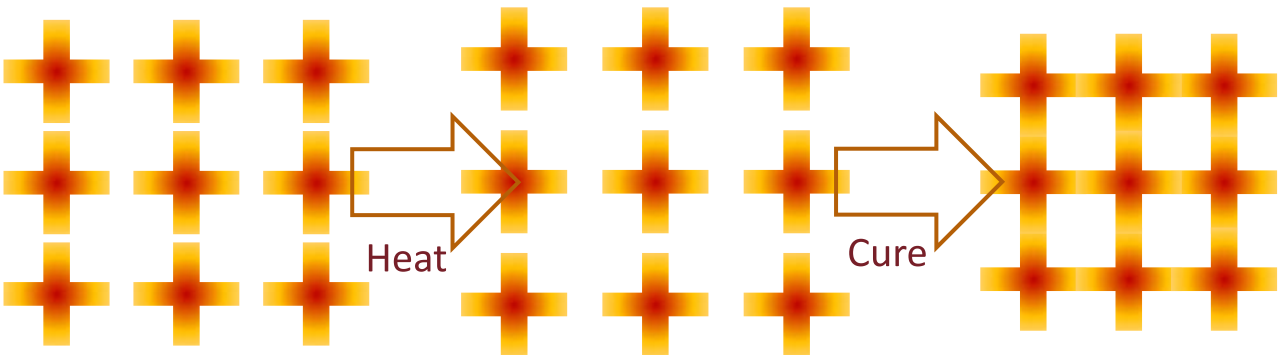
"LECy"



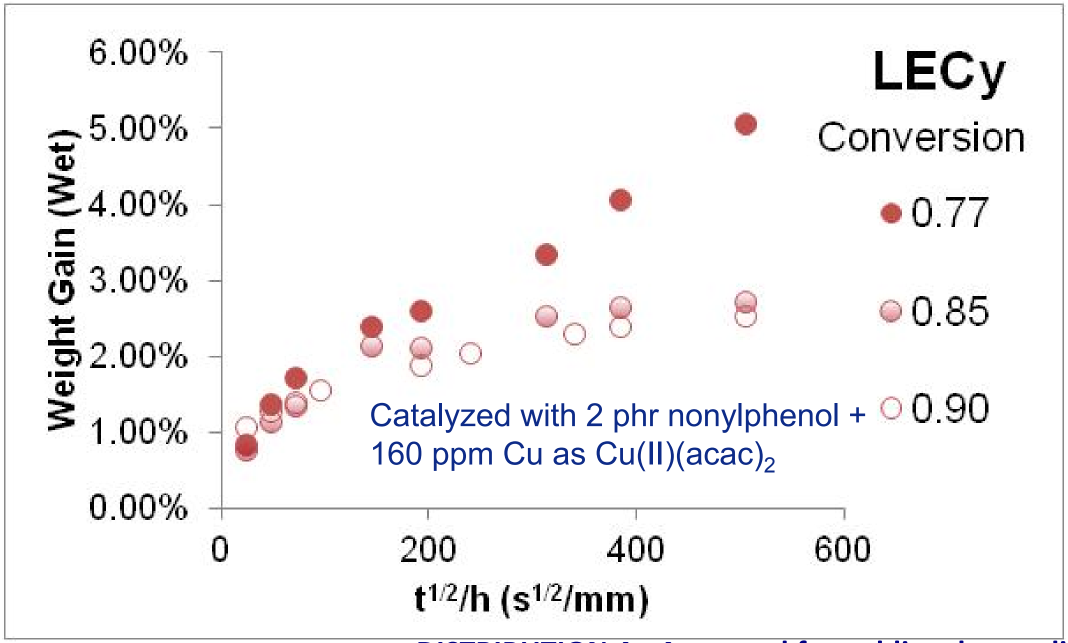
- In addition to glass transition temperature, many properties, such as density and water uptake, are mainly functions of conversion and monomer type

Basic Understanding of Moisture Uptake in Highly Cross-linked Networks

Main Stage Thermal Cure

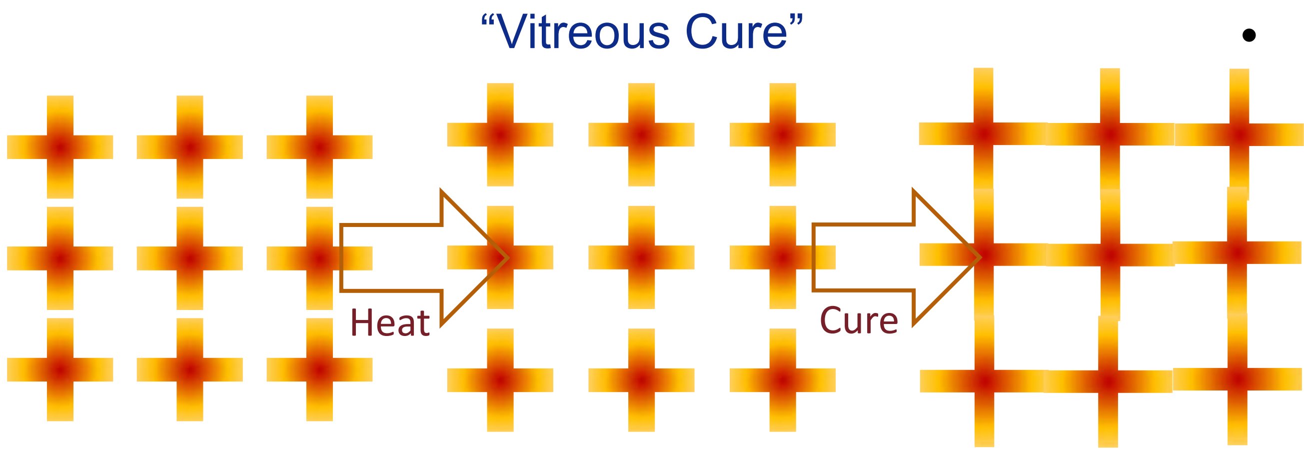


- Cure results in:
  - *Net Shrinkage*
  - *Less permeability*
  - *Higher modulus*
  - *Brittleness*

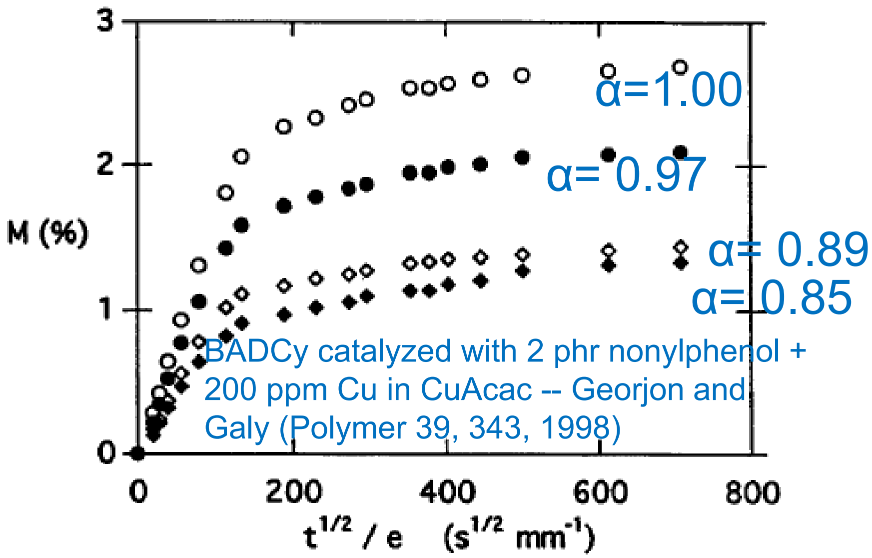


- Increasing conversion joins together more "loose ends" in the network, eliminating free space where water can be absorbed, therefore water uptake is expected to decrease with increasing conversion

Proposed Role of Vitrification in Controlling Moisture Uptake

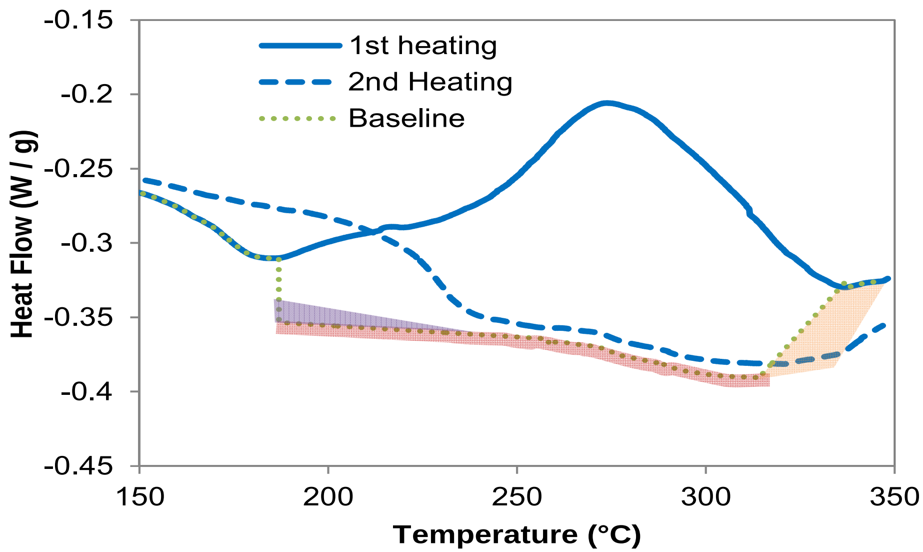


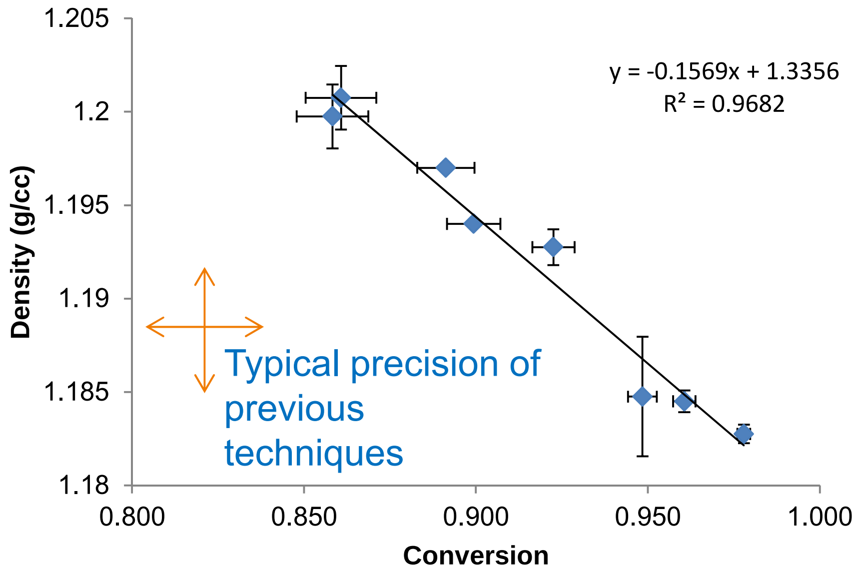
- Cure results in:
  - *Net Expansion*
  - *Higher permeability*
  - *Lower modulus*
  - *Toughness*



- Increasing conversions join "loose ends", but in the process they "freeze" the individual molecular centers-of-mass in place, resulting in exactly the opposite of the effects predicted by the traditional picture.

New Tools for Understanding Network Structure



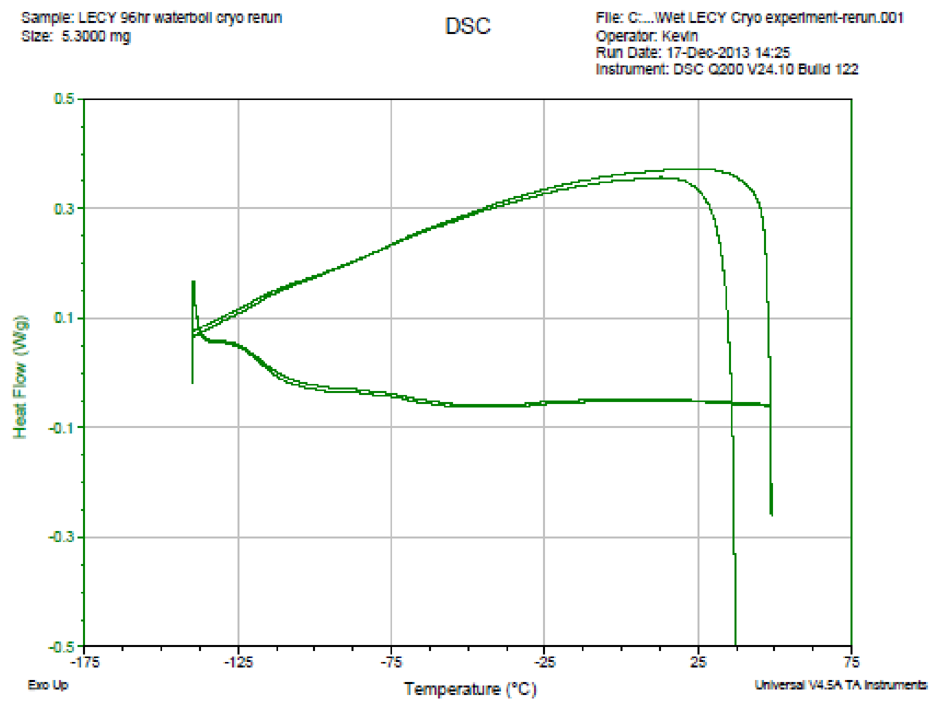


Typical computed DSC baseline with estimated zones of uncertainty

BADCy catalyzed with 2 phr nonylphenol + 160 ppm Cu in Cu(II)Acac: dV_m/dn_{tr} = 46 ± 4 cc/mol vs. previously determined value (2012) of 37 ± 15 cc/mol

- New DSC method allows for more precise and objective assessment of conversion, combined with T_G assessment for determination of conversion to within 0.01.
- New density technique adapted for use by Mr. Michael Ford allows for 100x faster assessment with high precision.

DSC Shows No Freezing of Water in Polycyanurate Networks



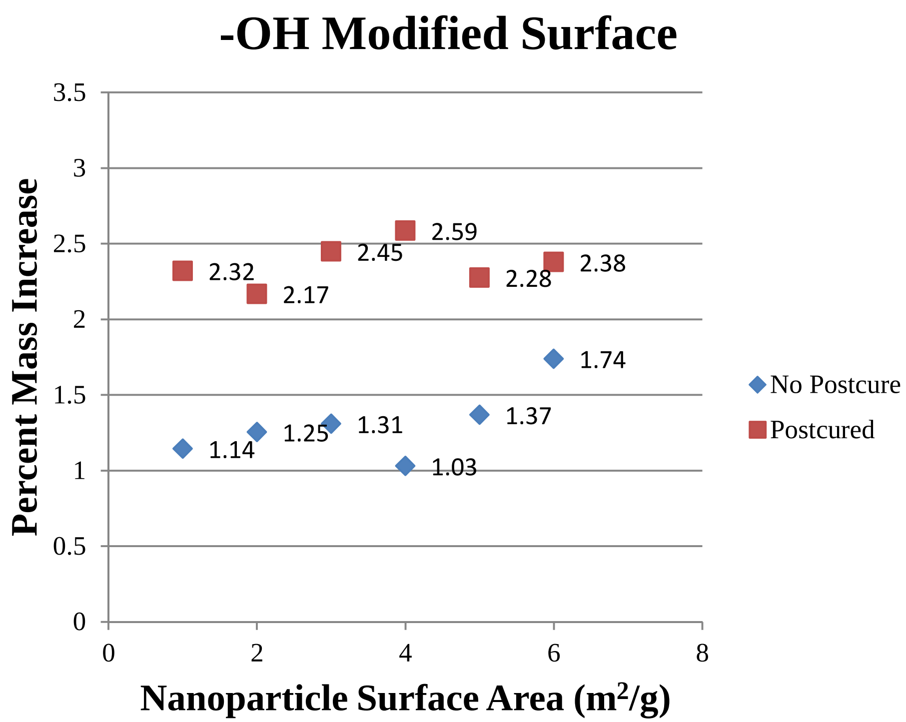
- In accordance with properties of water in cyanurate networks (i.e. higher miscibility at lower temperatures, no clustering)
- Recent NASA study of cryogenic toughness of cyanate ester / carbon fiber composites showed that residual stress minimization (by minimization of cure temperature) was the most important factor in achieving good toughness at cryogenic temperatures

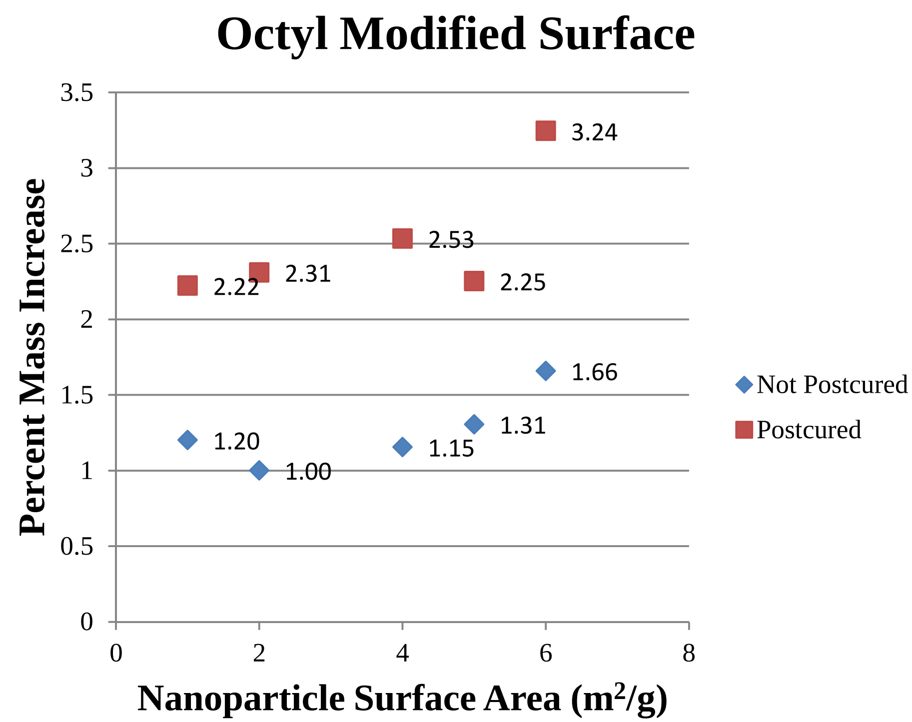
Moisture Uptake Is Likely a Minor Influence on Cryogenic Toughness

Material	B - Thickness		W - Height		a - Notch + Crack Length		P_Q - Applied Load		K_q (K_{1c})	
Specimen ID	(in)	(mm)	(in)	(mm)	(in)	(mm)	(lbf)	(N)	(psi-in$^{1/2}$)	(MPa-m$^{1/2}$)
Catalyzed LECy Panel Cured 1-6-14 Water Soaked-Tested 4-16-14										
STL300-1	0.1429	3.630	0.3920	9.957	0.1895	4.813	24.24	107.8	2,739	3.01
STL300-2	0.1456	3.698	0.4270	10.85	0.1985	5.042	27.70	123.2	2,782	3.06
STL300-3	0.1452	3.688	0.4280	10.87	0.2150	5.461	19.89	88.47	2,247	2.47
STL300-4	0.1508	3.830	0.4640	11.79	0.2195	5.575	27.76	123.5	2,647	2.91
STL300-5	0.1423	3.614	0.4310	10.95	0.2115	5.372	27.67	123.1	3,064	3.37
								Average	2,696	2.96
Catalyzed LECy (1-10-14) Tested 4-17-14										
STL300-6	0.1413	3.589	0.3575	9.081	0.1815	4.610	22.30	99.19	2,881	3.17
STL300-7	0.1472	3.739	0.3335	8.471	0.1810	4.597	19.89	88.47	2,868	3.15
STL300-8	0.1424	3.617	0.3545	9.004	0.1625	4.128	21.75	96.74	2,404	2.64
STL300-9	0.1408	3.576	0.3575	9.081	0.1710	4.343	27.20	120.99	3,216	3.53
STL300-10	0.1425	3.620	0.3520	8.941	0.1605	4.077	19.82	88.16	2,181	2.40
								Average	2,710	2.98

- LECy samples were soaked for 28 days at room temperature so as to maximize water uptake (1.5 wt%) while minimizing carbamate formation ($\Delta V/V$ ~ 0.2%).
- No significant difference between exposed and control samples in fracture toughness at RT; same glassy state dynamics should apply at cryogenic temperatures
- The water in cyanate ester networks appears to be neither clustered nor strongly bound

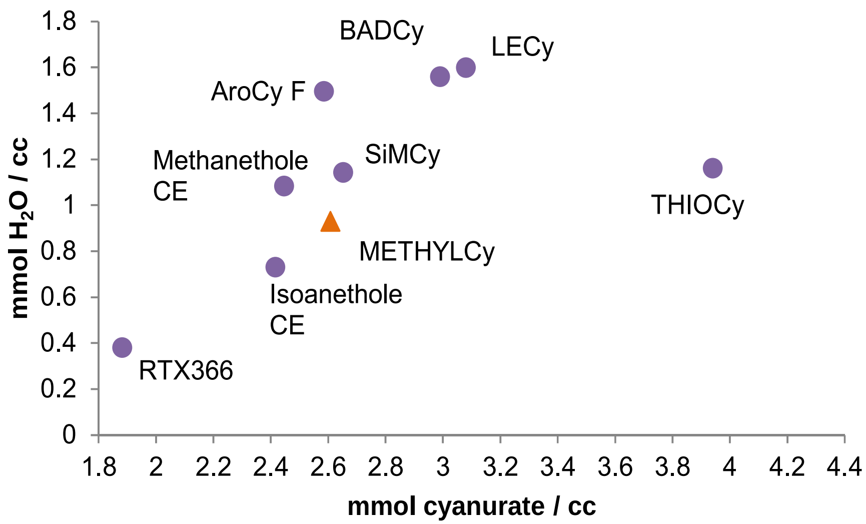
Nanoscale Reinforcement and Interphases

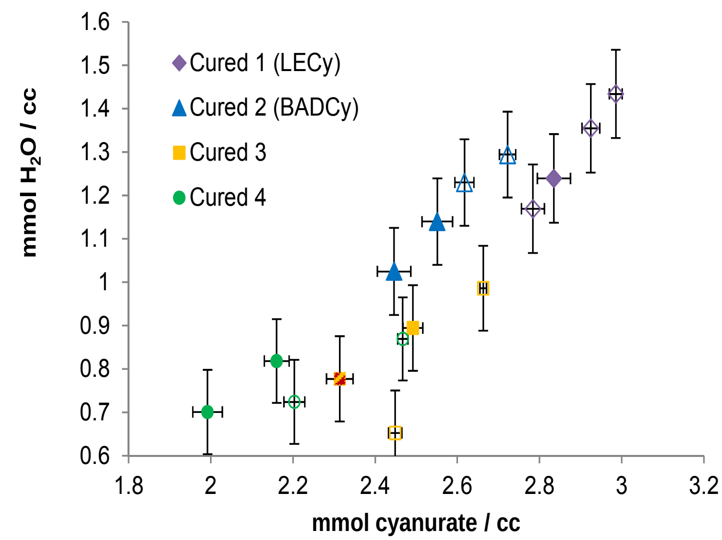


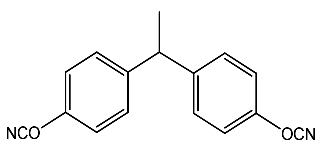


- A slight amount of water does accumulate at hydrophilic interphases in cyanate esters, but other effects such as poor bonding and damage tend to overwhelm these effects
- Nanoscale reinforcements such as graphene oxide with extreme water transport characteristics can alter the water uptake significantly.
- Generally speaking, blends and co-networks tend to follow linear rules of mixtures

Effect of Cyanurate Density on Moisture Uptake







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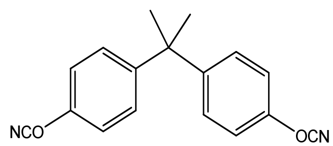

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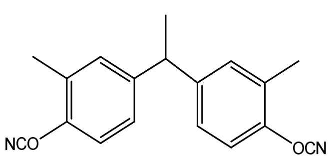

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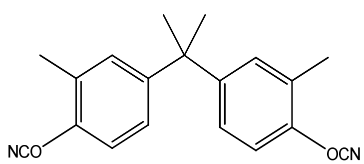
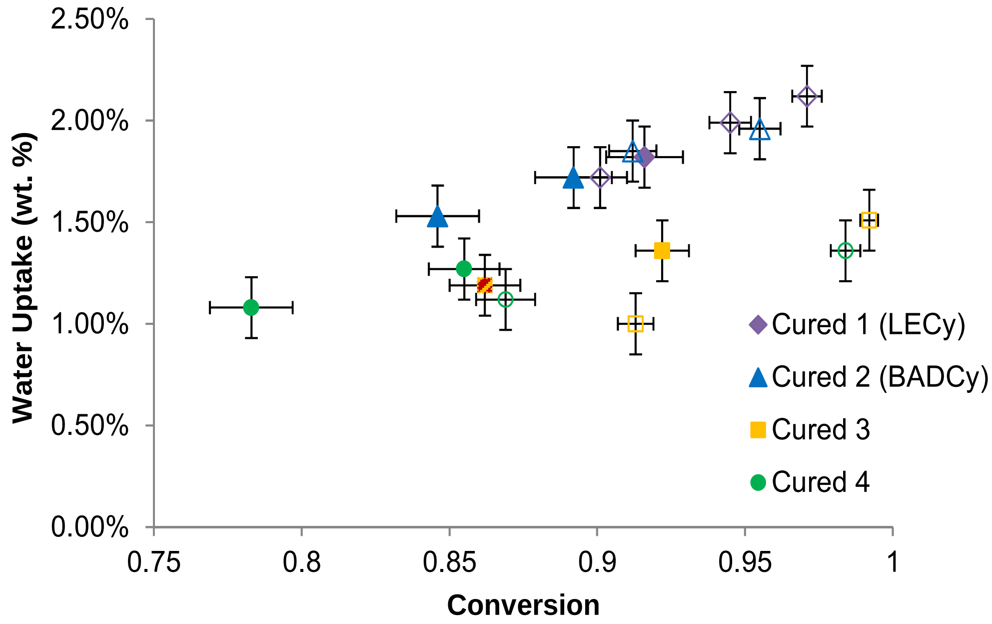
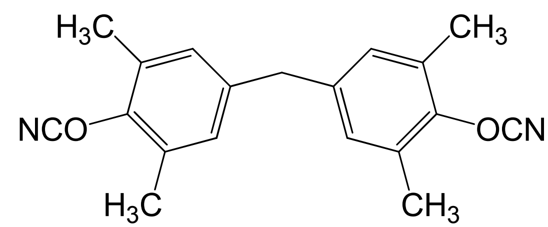


4

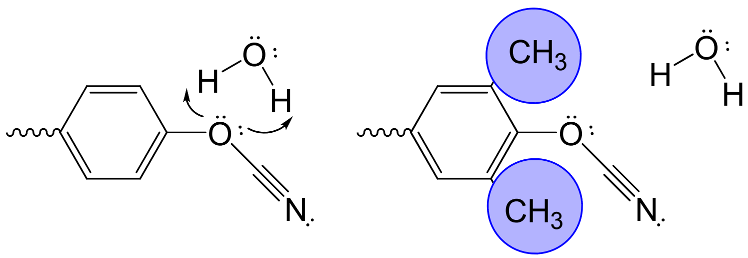
- Each monomer has a different water uptake as a function of cyanurate density, although all show an increasing trend
- The free volume / cyanurate density relationships are similar for all monomers

Effect of Methylation on Moisture Uptake



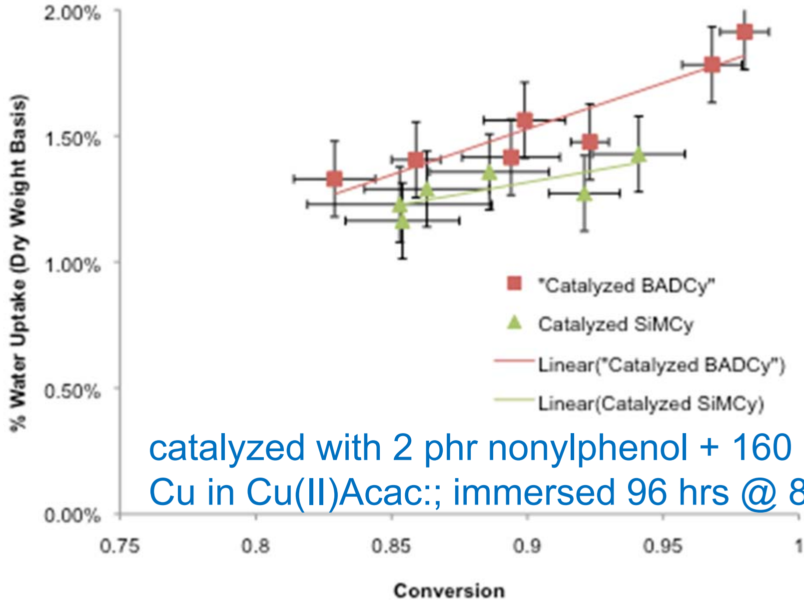


"METHYLCy"

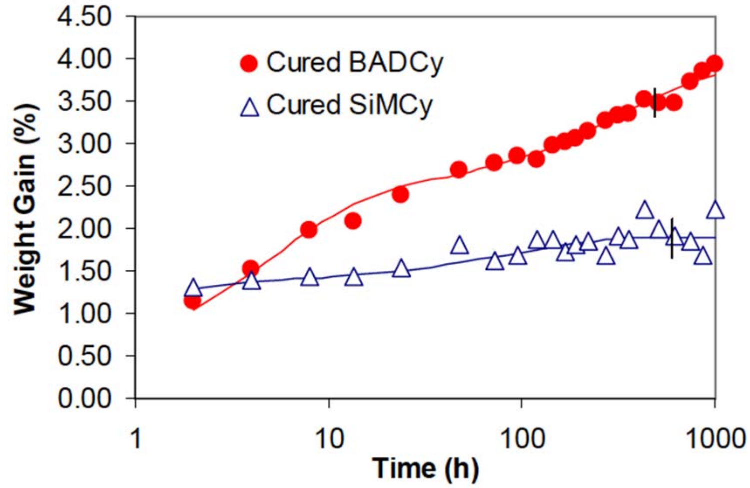


- Addition of a methyl group near the cyanurate oxygen causes a significant reduction in the tendency of moisture uptake to increase at high conversions
- Addition of a methyl group far from the cyanurate oxygen has no effect on water uptake as a function of conversion
- Methyl groups near the cyanurate oxygen block the favored sites for water uptake
- Vitrification appears not to influence the results

Effect of Silicon Substitution on Moisture Uptake



catalyzed with 2 phr nonylphenol + 160 ppm Cu in Cu(II)Acac:; immersed 96 hrs @ 85 °C



No catalyst; from Guenthner et al., *Macromolecules* **2006** *39*, 6046.

- Substitution of a silicon atom for a carbon atom in di(cyanate ester) network segments reduces moisture uptake by up to 50%
- In the corresponding tri(cyanate ester) networks, the same substitution increases moisture uptake by ~100% (i.e. effect is not intrinsic property of Si atom)
- Differences in vitrification also do not explain these effects, as they cause little change in moisture uptake

Summary: Basic Studies of Moisture Uptake in Cyanate Ester Networks

- **Many aspects of moisture uptake (and its minimization) in thermosetting polymer networks have been clarified through recent research efforts at AFRL/RQRP**
- **New tools and techniques for quantifying structure and properties of thermosetting networks have allowed for significant new insights into structure-property relationships in thermosetting networks**
- **Several unresolved issues relating to our understanding of moisture uptake in cyanate ester networks remain; approaches based on molecular modeling may provide insights leading to significant application payoffs**


QUESTIONS?
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